TITLE OF THE INVENTION

ORGANIC ELECTROLUMINESCENT DEVICE

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

5   The present invention relates to an organic

electroluminescent device utilizing an electroluminescent

phenomenon produced in organic substances, more particularly

to a device which is configured to interpose an organic

luminescent medium-containing layer between a positive

10   electrode and a negative electrode and designed to emit

light when an electric field is applied thereto.

DESCRIPTION OF RELATED ART

       An organic electroluminescent (may be hereinafter

referred to as EL) is formed of a thin film containing an

15   organic fluorescent material interposed between positive and

negative electrodes, and is such designed that a hole and an

electron are injected into the thin film where they

recombine to create an electron excited state, such as an

exiton. As this excited state is deactivated, light

20   emission occurs (by fluorescence, phosphorescence, delayed

fluorescence, luminescent phenomena accompanying transport

of energy, or the like). The organic EL device emits light

utilizing this mechanism.

       Characteristically, the organic EL device is capable of

25   planar light emission with a high level of luminance ranging

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from 100 to 10,000 cd/m^2 when the applied voltage is about 10 volts. Also, different emission hues, from blue to red, can be obtained by selecting the type of the organic fluorescent material used in the organic EL device.

5   The improvement in emission efficiency of the organic EL device can be achieved by increasing the efficiency of electron injection, and the use of low work function metals or their alloys for negative electrode materials have been attempted to increase the electron injection efficiency. In 10   U.S. Patent No. 4,885,211 and Japanese Patent Laying-Open No. Hei 2-15595, for example, a negative electrode material is disclosed which contains at least 50 atomic % of Mg and at least 0.1 atomic % of metal having a work function of at least 4.0 eV. Japanese Patent Laying-Open No. Hei 8-209120 15   discloses the use for a negative electrode of an alloy formed of 0.005 - 10 % by mass of an alkaline metal and a second metal. Japanese Patent Laying-Open No. Hei 9-232079 discloses a negative electrode material formed of an alloy which contains, by a total amount, 0.5 - 5 atomic % of an 20   alkaline metal or an alkaline earth metal having a work function of up to 2.9 eV. Japanese Patent Laying-Open No. Hei 10-12381 discloses the use of a ternary alloy for a negative electrode material, which contains 1 - 30 atomic % of a metal having a work function of at least 4.0 eV, 0.002 25   - 2.0 atomic % of Li, and the balance of Mg.

However, the conventional techniques such as described in the above-cited references use negative electrode materials containing extremely lower work function metals, i.e., metals having higher tendencies to release electrons.

5 When exposed to moisture or oxygen present in the air, such materials readily undergo oxidation to result in the accelerated deterioration of the negative electrodes. This has led to such problems as luminance reduction, build-up of operating voltage, formation and expansion of nonradiative

10 regions called "dark spots".

SUMMARY OF THE INVENTION

An object of the present invention is to provide an organic electroluminescent device which, due to its utilization of a specific negative electrode material, can

15 exhibit high levels of emission efficiency and emissive luminance and suppress a luminance drop during a long-term operation.

In accordance with a first aspect of the present invention, an organic electroluminescent device has a

20 luminescent material-containing layer interposed between a positive electrode and a negative electrode, and is designed to supply an electrical energy to the luminescent material that emits light upon receipt of the energy. The negative electrode characteristically contains at least one element,

25 "f", selected from elements having electronegativity values

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greater than that of calcium (Pauling electronegativity value = 1.0) and equal to or less than that of vanadium (Pauling electronegativity value = 1.6), and at least one element, "p", selected from elements having electronegativity values equal to or greater than that of aluminum (Pauling electronegativity value = 1.5).

Examples of useful "f" elements include Be (1.5), Sc (1.3), Ti (1.5), V (1.6), Cr (1.6), Mn (1.5), Y (1.2), Zr (1.4), Nb (1.6), La (1.1), Ce (1.1 - 1.2), Pr (1.1 - 1.2), Nd (1.1 - 1.2), Sm (1.1 - 1.2), Eu (1.1 - 1.2), Gd (1.1 - 1.2), Tb (1.1 - 1.2), Dy (1.1 - 1.2), Ho (1.1 - 1.2), Er (1.1 - 1.2), Tm (1.1 - 1.2), Yb (1.1 - 1.3), Lu (1.1 - 1.3), Hf (1.3) and Ta (1.5), wherein numerical values given in parentheses represent Pauling electronegativity values listed in a literature.

Examples of useful "p" elements include H (2.1), B (2.0), C (2.5), N (3.0), O (3.5), F (4.0), Al (1.5), Si (1.8), P (2.1), S (2.5), Cl (3.0), Ga (1.6), Ge (1.8), As (2.0), Se (2.4), Br (2.8), In (1.7), Sn (1.8), Sb (1.9), Te (2.1), I (2.5), Tl (1.8), Pb (1.8), Bi (1.9), Zn (1.6), Cd (1.7) and Hg (1.9), wherein numerical values given in parentheses represent Pauling electronegativity values listed in a literature.

In accordance with a second aspect of the present invention, an organic electroluminescent device has a

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luminescent material-containing layer interposed between a positive electrode and a negative electrode, and is designed to supply an electrical energy to the luminescent material that emits light upon receipt of the energy. The negative

5 electrode characteristically contains at least one element, "f", selected from elements having electronegativity values greater than that of calcium (Pauling electronegativity value = 1.0) and equal to or less than that of vanadium (Pauling electronegativity value = 1.6), at least one

10 element, "p", selected from elements having electronegativity values equal to or greater than that of aluminum (Pauling electronegativity value = 1.5), and at least one element, "d", selected from elements having electronegativity values equal to or greater than any of those of iron (Pauling

15 electronegativity value = 1.6), cobalt (Pauling electronegativity value = 1.6) and nickel (Pauling electronegativity value = 1.6) and equal to or less than that of gold (Pauling electronegativity value = 2.4), wherein the "d" element selected is the element that is

20 excluded from the selection of the "f" or "p" element.

Examples of useful "d" elements include Mo (1.8), Re (1.9), Fe (1.8), Ru (2.2), Os (2.2), Co (1.8), Rh (2.2), Ir (2.2), Ni (1.8), Pd (2.2), Pt (2.2), Cu (1.9), Ag (1.9), Au (2.4), Hg (1.9), B (2.0), Tl (1.8), Si (1.8), Ge (1.8), Sn

25 (1.8), Pb (1.8), P (2.1), As (2.0), Sb (1.9), Bi (1.9), Se

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(2.4) and Te (2.1), wherein numerical values given in parentheses indicate Pauling electronegativity values listed in a literature.

In a third aspect of the present invention, the element, "p", as used in the aforementioned first and second aspects, is selected from elements having electronegativity values equal to or greater than that of aluminum (Pauling electronegativity value = 1.5), less than that of carbon (Pauling electronegativity value = 2.5), and less than that of iodine (Pauling electronegativity value = 2.5).

It is preferably that those elements, "f", "p" and "d", are selected from different groups in the periodic table, respectively. A preferred element content of the negative electrode material is in the range of 0.1 - 10 % by mass (more preferably in the range of 0.3 - 3 % by mass) for the "f" element, in the range of 0.1 - 99.5 % by mass for the "p" element, and in the range of 0 - 99.8 % by mass for the "d" element. When the three elements, "f", "p" and "d", are all contained in the negative electrode material, it is preferred that a sum of the "p" and "d" element contents is not below 90 % by mass.

In a fourth aspect of the present invention, the luminescent material-containing layer, as used in the first through third aspects, contains at least a host as a principal constituent and a fluorescent dopant. A ratio in

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molar mass of the dopant molecule to the host molecule
(dopant/host) is generally in the range of 0.344 - 2.90,
preferably in the range of 0.441 - 2.26.

In a fifth aspect of the present invention, the "f" is
at least one element selected from elements which have
electronegativity values greater than that of calcium
(Pauling electronegativity value = 1.0), and, less than that
of zirconium (Pauling electronegativity value = 1.4) and
which, in the form of simple substance, have melting points
higher than that of lithium (literature-listed melting point
= 180.5 °C), and, equal to or lower than that of lutetium
(literature-listed melting point = 1,660 °C). Specifically,
the "f" is at least one element selected from Sc (1,540 °C),
Y (1,520 °C), La (921 °C), Ce (799 °C), Pr (931 °C), Nd
(1,020 °C), Sm (1,080 °C), Eu (822 °C), Gd (1,310 °C), Tb
(1,360 °C), Dy (1,410 °C), Ho (1,470 °C), Er (1,530 °C), Tm
(1,550 °C), Yb (819 °C) and Lu (1,660 °C), wherein numerical
values given in parentheses represent melting points of
their simple substances as listed in a literature.

In a sixth aspect of the present invention, the "f" is
the element whose simple substance has a melting point of
lower than that of Sc (1,540 °C). Specifically, the "f" is
at least one element selected from Y, La, Ce, Pr, Nd, Sm,
Eu, Gd, Tb, Dy, Ho, Er and Yb. These "f" elements are
particularly suitable when negative electrodes are formed by

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a resistance-heat or electron-beam vapor deposition technique.

In a seventh aspect of the present invention, the "f" is the element whose simple substance has a melting point of below 1,000 °C. Specifically, the "f" is at least one element selected from La, Ce, Pr, Eu and Yb. These "f" elements are particularly suitable when negative electrodes are formed by a resistance-heat vapor deposition technique.

In an eighth aspect of the present invention, the "f" is the element whose simple substance has a boiling point equal to or lower than that of Ce or Lu, and, equal to or higher than that of Dy. Specifically, the "f" is at least one element selected from Sc (2,830 °C), Y (3,300 °C), Ce (3,400 °C), Pr (3,000 °C), Nd (3,100 °C), Gd (3,300 °C), Tb (3,100 °C), Dy (2,560 °C), Ho (2,690 °C), Er (2,860 °C) and Lu (3,400 °C), wherein numerical values given in parentheses represent boiling points of their simple substances as listed in a literature. The "f" element is selected preferably from lanthanum series elements, more preferably from cerium group elements with atomic numbers 57 through 62 (La ~ Sm). These "f" elements are suitable when negative electrodes are formed by a resistance-heat vapor deposition technique, and are particularly suitable when negative electrodes are sputter formed.

In a ninth aspect of the present invention, the "f" is

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the element whose simple substance has a boiling point

equal to or lower than that of Tm. Specifically, the "f" is

at least one element selected from Sm (1,790 $^{\circ}$C), Eu (1,600

$^{\circ}$C), Tm (1,950 $^{\circ}$C) and Yb (1,194 $^{\circ}$C), wherein numerical

5   values given in parentheses represent melting points of

their simple substances as listed in a literature.

Preferbly, the "f" is the element whose simple substance has

a boiling point equal to or higher than that of Eu. These

"f" elements are suitable when negative electrodes are formed

10   by a resistance heat vapor deposition technique, and are

particularly suitable when negative electrodes are formed by

an electron-beam vapor deposition technique.

In a tenth aspect of the present invention, the "f" is

the element whose simple substance has a metallic bond

15   radius equal to or smaller than that of cerium, and, equal

to or larger than that of thulium or lutetium.

Specifically, the "f" is at least one element selected from

Ce (0.183 nm), Pr (0.182 nm), Nd (0.181 nm), Sm (0.179 nm),

Gd (0.179 nm), Tb (0.176 nm), Dy (0.175 nm), Ho (0.174 nm),

20   Er (0.173 nm), Tm (0.172 nm) and Lu (0.172 nm), wherein

numerical values given in parentheses indicate metallic bond

radii of their simple substances as listed in a literature.

In an eleventh aspect of the present invention, the "p"

is at least one element selected from Zn, B, Al, In, Tl, Si,

25   Ge, Sn, P, Sb, Bi, S, Se and Te.

In a twelfth aspect of the present invention, the "d" is the transition metal element whose simple substance has a melting point lower than that of Mo (2,620 °C). Specifically, the "d" is at least one element selected from

5 Fe (1,540 °C), Ru (2,310 °C), Co (1,490 °C), Rh (1,970 °C), Ir (2,410 °C), Ni (1,450 °C), Pd (1,550 °C), Pt (1,770 °C), Cu (1,083 °C), Ag (962 °C) and Au (1,064 °C), wherein numerical values given in parentheses indicate melting points of their respective simple substances as listed in a

10 literature.

In a thirteenth aspect of the present invention, the "p" element is Al, while the "d" is the element whose simple substance has a boiling point equal to or lower than that of Co, and, equal to or higher than that of Ag. Specifically,

15 the "d" is at least one element selected from Co (2,870 °C), Ni (2,730 °C), Cu (2,570 °C) and Ag (2,210 °C), wherein numerical values given in parentheses indicate boiling points of their respective simple substances as listed in a literature.

20 Al, if used as the "p" element, melts and vaporizes at temperatures respectively lower than the melting point (660.4 °C) and boiling point (2,470 °C) of its simple substance. This effectively facilitates formation of negative electrodes by a vacuum vapor deposition technique.

25 Also, Al, if existing in the form of a simple substance, has

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the following physical properties; electrical resistivity =
2.655 $\mu\Omega$cm, thermal conductivity = 237 W/m·K, Young's
modulus = 68.3 GN/m^2 and coefficient of linear expansion =
0.237 x 10^{-4}/K. Accordingly, the Al-containing negative

5   electrodes exhibit excellent electrical and thermal
conductivities, as well as appropriate levels of mechanical
strength.

In a fourteenth aspect of the present invention, the "p"
element is Sb, while the "d" is the element whose simple

10   substance has a thermal conductivity equal to or higher than
that of Al. Specifically, the "d" is at least one element
selected from Ag (427 W/m·K), Cu (398 W/m·K), Au (315 W/m·K)
and Al (237 W/m·K), wherein numerical values given in
parentheses indicate thermal conductivities of their

15   respective simple substances as listed in a literature.

Sb, if used as the "p" element, melts and vaporizes at
temperatures respectively lower than the melting point
(630.7 °C) and boiling point (1,750 °C) of its simple
substance. This effectively facilitates formation of

20   negative electrodes by a vacuum vapor deposition technique.
Also, Sb, if existing in the form of simple substance, has
the following physical properties; Young's modulus = 77.9
GN/m^2 and coefficient of linear expansion = 0.172 x 10^{-4}/K
(parallel to a c-axis) and 0.080 x 10^{-4}/K (perpendicular to a

25   c-axis). By the same reason as applied to Al, the Sb-

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containing negative electrodes exhibit appropriate levels of mechanical strength. Sb, if in the form of simple substance, also has the following physical properties; electrical resistivity = 39.6 $\mu\Omega$cm and thermal conductivity

5   = 24.3 W/m·K. Accordingly, when desired to obtain negative electrodes having excellent electrical conductivities and excellent heat dissipating properties through heat conduction, Sb, as the "p" element, may preferably be used in combination with the other element whose simple substance

10   has the reduced electrical resistivity and the increased thermal conductivity. Examples of such elements for use in combination with Sb are below listed with their respective physical properties measured when in the form of simple substance; Ag (electrical resistivity = 1.59 $\mu\Omega$cm, Young's

15   modulus = 76 GN/m^2 and coefficient of linear expansion = 0.193 x 10^{-4}/K), Cu (electrical resistivity = 1.67 $\mu\Omega$cm (20 °C), Young's modulus = 110 GN/m^2 and coefficient of linear expansion = 0.162 x 10^{-4}/K) and Au (electrical resistivity = 2.35 $\mu\Omega$cm, Young's modulus = 80 GN/m^2 and coefficient of

20   linear expansion = 0.142 x 10^{-4}/K).

In a fifteenth aspect of the present invention, the "p" element is Bi, while the "d" is the metallic element whose simple substance has a thermal conductivity equal to or higher than that of Au. Specifically, the "d" is at least

25   one element selected from Ag, Cu and Au.

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Bi, if used as the "p" element, melts and vaporizes at temperatures respectively lower than the melting point (271.3 °C) and boiling point (1,560 °C) of its simple substance. This effectively facilitates formation of

5   negative electrodes by a vacuum vapor deposition technique. Also, Bi, if existing in the form of simple substance, has the following physical properties; Young's modulus = 31.7 GN/m^2, coefficient of linear expansion = 0.162 x $10^{-4}/K$ (parallel to a c-axis) and 0.120 x $10^{-4}/K$ (perpendicular to a

10   c-axis). By the same reason as applied to Al and Sb, the Bi-containing negative electrodes exhibit appropriate levels of mechanical strength. Bi, if in the form of simple substance, also has the following physical properties; electrical resistivity = 107 $\mu \Omega$ cm and thermal conductivity

15   = 9.15 W/m·K (perpendicular to a c-axis). Accordingly, when desired to obtain negative electrodes having excellent electrical conductivities and excellent heat dissipating properties via heat conduction, Bi, as the "p" element, may preferably be used in combination with the other element

20   whose simple substance has the reduced electrical resistivity and the increased thermal conductivity compared to the "p" element.

In a sixteenth aspect of the present invention, a mean electronegativity value E_{ave}, as calculated from weighting an

25   electronegativity value of each element constituting a

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negative electrode by a proportion in number of its atoms present in the negative electrode, is in the range of 1.50 - 1.91, assuming that an electronegativity value of a lanthanoid element (Ln), such as Ce, is 1.15. The mean

5   electronegativity value E_{ave} is preferably in the range of 1.50 - 1.59 or 1.80 - 1.91.

In a seventeenth aspect of the present invention, when a flow of an DC current drives the device to emit light with a controlled luminance of 100 cd/m^2, an emission efficiency,

10   as calculated by dividing the luminance by a current density, is not below 10.0 cd/A.

In accordance with a eighteenth aspect of the present invention, an organic electroluminescent device has a luminescent material-containing layer interposed between a

15   positive electrode and a negative electrode, and is designed to supply an electrical energy to the luminescent material that emits light upon receipt of the energy. The negative electrode contains "f" and "p" elements. The "f" is the element whose simple substance has a metallic bond radius

20   equal to or larger than that of Ce, and, equal to or smaller than that of Eu or Yb. Specifically, the "f" is at least one element selected from La (0.187 nm), Ce (0.183 nm), Eu (0.198 nm) and Yb (0.194 nm), wherein numerical values given in parentheses indicate metallic bond radii of their simple

25   substances as listed in a literature. The "p" is the element

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whose simple substance has a melting point equal to or lower than that of Al (melting point = 660.4 ℃), and, equal to or higher than that of Sn (melting point = 231.97 ℃), as well as having a modulus of elasticity intension, i.e., Young's

5   modulus equal to or higher than that of Sn, and, equal to or lower than that of Zn. Specifically, the "p" is at least one element selected from Zn (96.5 GN/m^2), Al (68.3 GN/m^2), Sn (41.4 GN/m^2) and Sb (77.9 GN/m^2), wherein numerical values given in parentheses indicate Young's moduli of their simple

10   substances as listed in a literature.

      In an nineteenth aspect of the present invention, the "f" and "p" elements, as used in the aforementioned 18th aspect, are Ce and Al, respectively.

      In accordance with a twentieth aspect of the present

15   invention, the negative electrode, as used in the preceding 1st, 3rd through 11th and 16th through 19th aspects, includes a first layer closest to the luminescent material-containing layer, a second layer overlying the first layer and a third layer overlying the second layer. The first

20   negative electrode layer is substantially formed from the "f" element, the second negative electrode layer from a mixture or compound of the "f" and "p" elements, and the third negative electrode layer from the "p" element.

      In accordance with the twenty-first aspect of the

25   present invention, the second negative electrode layer, as

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used in the aforementioned 20th aspect, has a composition gradient in its thickness direction such that toward its interface with the third negative electrode layer from its interface with the first negative electrode layer, its "f"

5   element content decreases while its "p" element content increases.

Such a composition graded structure of the second negative electrode layer not only contributes to the improved interlaminar adhesion between the first and second

10   negative electrode layers and between the second and third negative electrode layers, but also serves to relax a thermal shock due to a difference in thermal expansivity between the first and third negative electrode layers.

In accordance with the twenty-second aspect of the

15   present invention, at least one of the first, second and third negative electrode layers, as respectively used in the 20th aspect of the present invention, contains an additional element different from the constituent element thereof.

A high level of emission efficiency is realized by the

20   organic EL device according to the present invention. For example, when the organic EL device is driven by a flow of an DC current to emit light with a luminance of 100 cd/m^2, it can exhibit an emission efficiency of not below 7.0 cd/A, further of not below 10.0 cd/A, as calculated by dividing

25   the luminance by a current density. Furthermore, the

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organic EL device can be obtained which exhibits an emission efficiency of not below 5.0 ℓm/w, further of not below 10.0 ℓm/w, as calculated by dividing a luminous flux emitted therefrom by an input power applied thereto.

5   A high level of luminance is also realized by the organic EL device according to the present invention. For example, the organic EL device can be obtained which exhibits an emissive luminance L_{5V} of not below 250 cd/m^2, further of not below 500 cd/m^2, when the applied voltage is

10   5 volts.

Also in accordance with the present invention, a luminance drop during a long-term operation can be suppressed. For example, the organic EL device can be obtained which, when its operation by an DC constant current

15   is started from an initial luminance of 500 cd/m^2 and continued until a current density converges to a constant value, exhibits a luminance ratio R_{500h}, as calculated by a ratio of the initial luminance to a luminance after the lapse of 500 hours, of not below 10 %, further of not below

20   50 %.

A definition of electronegativity was proposed by Pauling and alternatively by Mulliken, and have been modified to date by their successors. The electronegativity values according to the Pauling scale is used throughout the

25   specification of this application. However, this is not

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intended to exclude the use of other scales, such as the

Mulliken electronegativity scale, as a selection reference

of elements for use in the practice of the present

invention, since they are approximately in line with each

5   other. The electronegativity is a parameter as a measure of

the power of a bonding atom to attract electrons to itself.

The greater the difference in electronegativity between two

atoms that form a bond, the more likely one atom attracts

electrons to itself. This results in an increased ionic

10   character in the bond. The electronegativity can also be

used as a measure of indicating an electro-donating or

electron-accepting property of an atom. The less

electronegative atom has a greater electro-donating

property, while the more electronegative atom has a stronger

15   electro-accepting property. The atom having an intermediate

electronegativity has an amphoteric property.

Electronegativity values for various elements are scaled by

Pauling or Mulliken. Although closely related to physical

properties of elements, the electronegativity is not a

20   physicochemical quantity such as mass or voltage, and thus

carries no unit.

If the Mulliken approach is applied, the value of

electronegativity (EN) of a given element can be determined

from its ionization energy (IE) and electron affinity (EA)

25   by using the following experimental equation;

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$$EN = (IE + EA)/(544 \text{ kJ} \cdot \text{mol}^{-1})$$

Also, if the Pauling approach is applied, the difference δE_{AB} in electronegativity between the two elements A and B in a compound AB can be obtained from the following equation;

$$\delta E_{AB} = 0.088[\{E_{real} - (E_{AA} \cdot E_{BB})^{0.5}\}/(\text{kJ} \cdot \text{mol}^{-1})]^{0.5}$$

where E_{real} is a measured value for a bond energy of a A-B bond formed between the two elements A and B, and E_{AA} and E_{BB} are measured values for bond enegies of A-A and B-B bonds, respectively.

For the compound AB, if the difference δE_{AB} in electronegativity between the elements A and B is zero, the A-B bond has a 100 % pure covalent character. If an absolute value of δE_{AB} is about 1.7, the A-B bond has 50 % ionic and 50 % covalent characters. If an absolute value of δE_{AB} is 2.0, the A-B bond has about 63 % ionic and about 37 % covalent characters, showing a marked ionic character. The followings illustrate proportions of ionic bonding property that indicate bonding properties of vaious hologen halide molecules, as estimated from measurements of dipole moments that exist in those molecules, and an absolute value of electronegativity difference δE_{HX} between hydrogen (H) and a halogen element (X) together constituting each of those hydrogen halide molecules; hydrogen iodide (ioninc bonding property = 4 %, $\delta E_{HI} = 0.4$), hydrogen bromide (ioninc bonding

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property = 11 %, δE_{HBr} = 0.7) and hydrogen chloride (ioninc

bonding property = 19 %, δE_{HCl} = 0.9).

In the manner as stated above, the electronegativity

can be used as an important indication when determining

5   bonding states between similar or dissimilar elements.

The concept of electronegativity is intrinsic to an

element. For example, diamond, graphite and amorphous

carbon are allotropic forms of carbon. They have the same

electronegativity value, regardless of their allotropic

10   forms. It is however pointed out that they have work

functions significantly different from each other.

Work function is an indicator as frequently used

heretofore when selecting elements for constituting a

negative electrode of an organic EL device. This work

15   function is a physicochemical quantity that varies sensively

depending upon the surface conditions of materials, and can

be an useful indicator if a collection of measured values

for individual materials is obtained. However, the use of

work function, as determined for each single element, as an

20   indicator for property prediction, such as of compounds or

mixtures consisting of plural elements, gives results that

are not considered to be very good. In the present

invention, the electronegativity, a characteristic value

intrinsic to an element, is used as a representative

25   indicator when selecting elements for constituting a

negative electrode. The electronegativity is a numerical representation of the power of an element atom to hold electrons using an integer or real number, and the present invention utilizes electronegativity values which indicate

5   element-intrinsic preperties, as representative indicators when selecting elements for constituting a negative electrode.

Alkaline or alkaline earth metals have been used to form negative electrodes, for the purpose of improving the

10   efficiency with which electrons are injected into an organic compound layer of an organic EL device. Examples of representing alkaline metals include Cs (0.7), Rb (0.8), K (0.8), Na (0.9) and Li (1.0), and examples of representing alkaline earth metals include Ba (0.9), Sr(1.0), Ca (1.0)

15   and the like, wherein numerical values given in paratheses indicate electronegativity values. All the alakaline metals used, as well as most of the alkaline earth metals used, have electronegativity values of not exceeding 1.0. Since such metals having electronegativity values of not exceeding

20   1.0 hold electrons very weakly, negative electrodes formed therefrom are readily subjected to oxidation and thus unstable. Also, those metals tend to form water-soluble ionic materials. Accordingly, the exposure thereof to an atmosphere results in the increased occurrence for them to

25   start liquefying from surfaces upon absorption of water

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vapor or moisture, called a deliquescent phenomenon, which
is a problem. For example, Fr, Cs, Rb, K and Na, members of
an alakline metal family, are readily oxidized by oxygen in
the air to change to their oxides. Li reacts with nitrogen

5   in the air to change to its nitride. Ra, Ba, Sr, Ca and Mg,
members of an alkaline earth metal family, are readily
oxidized by oxygen in the air to change to their oxides.
Fr, Cs, Rb, K, Na, Li, Ba, Sr and Ca also react with a cold
water or an atmospheric humid air to produce metal

10   hydroxides and a hydrogen gas.

All the simple salts formed from alakaline metals are
soluble in water. $LiNO_3$ and $NaNO_3$ are deliquescent, for
example.

In the present invention, a negative electrode at least

15   contains the "f" ~~elemen~~ element selected from those having
electronegativity values higher than that of calcium, and,
equal to or lower than that of vanadium, instead of the
aforementioned element having an electronegativity value of
not exceeding 1.0. An atom of the "f" element has an

20   appropriately low electron-holding power, so that efficient
injection of electrons can be achieved from a negative
electrode region containing the "f" element into an organic
compound layer of an organic EL device. Also, the atom
constituting the "f" element, if alone, is less subjected to

25   oxidation, compared to those having electronegativity values

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of not exceeding 1.0. Also, when the "f" element is combined

with the "p" element having an electronegativity value of not

below 1.5 to form a mixture or compound, oxidation and

following deterioration of the negative electrode formed

5   from the mixture or compound can be suppressed to such an

extent that its satisfactory performance is maintained.

This is explained by the following reason: The atom of the

"p" element having an electronegativity value of not below

1.5, preferably in the range of 1.5 - 2.4, has a higher

10   electron-holding power and the atom itself is relatively

less subjected to oxidation. Accordingly, the arrangement

of the "p" atoms to surround the "f" atoms protects the "f"

atoms from contacting oxidizing species, such as oxygen,

nitrogen and moisture.

15   Where the "f" element having an electronegativity value

higher than that of calcium, and, equal to or lower than

that of vanadium, together with the "p" element having an

electronegativity value equal to or higher than that of

aluminium, are included in a negative electrode, a

20   difference δE in electronegativity between the "f" and "p"

elements does not fall below 0.8, probably resulting in the

formation of the bond having a 15 % or higher ionic

character between the "f" and "p" atoms. Once such a bond has

been formed, it becomes unlikely that the "f" atoms are

25   further oxidized as by oxygen or moisture. It is thus

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expected that the "f" atoms maintain their predetermined state contemplated in the fabrication of the device. Also, selected combinations of the particular "f" and "p" elements result in preventing the reaction with atmospheric water

5   vapor, i.e., result in the reduced occurrence of a deliquescent phenomenon.

Besides the aforementioned "f" and "p" elements, an additional element, "d", having an electronegativity value equal to or higher than any of those of iron, cobalt and

10   nickel, and, equal to or lower than that of gold may futher be included in a negative electrode. The "d" element has an appropriately high electron-holding power, and its atom itself is very unlikely to be oxidized. Accordingly, the arrangement of the "d" atoms to surround the "f" atoms serves

15   to protect the "f" atoms from contacting oxidizing species, such as oxygen, nitrogen and moisture. Also, since the "d" element having an electronegativity value in the range of 1.8 - 2.4 has a higher tendency to produce a compound or mixture which exhibits a good electric or/and thermal

20   conductivity, a compound or mixture further containing the "d" element, besides the "f" and "p" elements, exhibit improved electrical or/and thermal conductivity.

Where the "f", "p" and "d" elements are respectively selected from different groups in the periodic table, a

25   compound or mixture containing these three different

-24-

elements possibly forms a material having a more complex structure than when containing the "f", "p" or "d" element alone, and exhibits new physical properties. Such new physical properties include the improved mechanical strength

5   resulting from the change in bonding state of atoms in the material and the increased chemical stability, for example.

As aforestated as the fourth aspect of the present invention, the luminescent material-containing layer may at least contain a host, as a principal constituent, and a

10   fluorescent dopant such that a ratio in molar mass of the dopant molecule to the host molecule (dopant/host) is generally in the range of 0.344 - 2.90, preferably in the range of 0.441 - 2.26. When such a composition is vapor deposited, those dopant and host molecules behave similarly

15   in a vapor phase, reach a substrate while forming a nearly perefectly mixed molecular beam in the vapor phase, and change to a solid phase. This enables formation of the luminescent material-containing layer (luminescent layer) from the nearly ideal mixture of the dopant and host

20   molecules. Therefore, the improvement in performance, particularly in emission efficiency, of the organic EL device can be achieved. Its service life can also be extended.

BRIEF DESCRIPTION OF THE DRAWINGS

25   Figure 1 is a sectional view, illustrating an

-25-

embodiment of an organic EL device in accordance with the

present invention; and

Figure 2 is a sectional view, illustrating another

embodiment of an organic EL device in accordance with the

5   present invention.

DESCRIPTION OF PREFERRED MBODIMENTS

A detailed description of the present invention is

below given with reference to specific embodiments and

examples of the present invention and comparative examples.

10   **EXAMPLE 1**

Figure 1 is a sectional view, showing a construction of

an organic EL device of Example 1. Referring to Figure 1, a

glass substrate 1 is shown to carry a transparent positive

electrode 2 thereon. In the fabrication of a display with

15   light emitting elements arranged in a matrix pattern, a

parallel set of strip-form transparent positive electrodes 2

may be pattern formed on the glass substrate 1. A sequence

of a hole injecting and transporting layer 3, a luminescent

layer 4 and an electron injecting and transporting layer 5,

20   each formed of organic material, overlies the patterned

transparent positive electrode 2. The hole injecting and

transporting layer 3, luminescent layer 4 and electron

injecting and transporting layer 5 constitute an organic EL

layer 8. Overlying the electron injecting and transporting

25   layer 5 is a negative electrode 6 covered with a protective

-26-

film 7.

A manufacturing process of the organic EL device of the present example will be now explained.

Formation of a tranparent positive electrode

A parallel set of stip-form transparent electrodes 2 is pattern formed on the glass substrate 1. An average thickness of the transparent electrodes 2 may be 140 nm, for example. It is generally maintained within the range of 70 nm - 3 μm, preferably within the range of 90 nm - 0.5 μm. Conductive materials generally used to form the transparent positive electrode 2 generally have work functions (WF) or ionization potentials (IP) from a solid state of about 4.6 eV or higher, and exmaples thereof include chalcogenide compounds such as indium tin oxide (ITO) and tin oxide (SnO_2), simple substances and compounds of metallic elements such as Co, Au, Ni, Pd and Pt. In this Example, the transparent positive electrode 2 was formed from indium tin oxide (ITO). Its ionization potential (IP) from a solid state was 4.7 eV, when measured under an atmospheric pressure according to a low energy electron counting method. Patterning of the transparent electrode 2 can be achieved by known techniques, such as a wet etching technique using an aqueous solution of hydrochloric acid containing $FeCl_3$.

For the purpose of removing any impurities that may be present thereon, as by oxidation or decomposition, the

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patterned positive electrode 2 is UV etched under the
oxygen-containing atmosphere until its clean surface is
exposed to outside. Since this cleaning process is a dry
process which does not use a solution, it is very unlikely

5   that the patterned positive electrode 2 is at its surface
recontaminated by impurities.

Formation of an organic EL layer

The hole injecting and transporting layer 3,
luminescent layer 4 and electron injecting and transporting

10   layer 5 are sequentially stacked on the glass substrate 1
carrying the transparent positive electrode 2 by a vacuum
vapor deposition technique. The hole injecting and
transporting layer 3, luminescent layer 4 and electron
injecting and transporting layer 5 are vapor deposited at a

15   surrounding pressure reduced to about 0.1 mPa at a substrate
temperature of 25 °C. The hole injecting and transporting
layer 3 was formed from 4, 4', 4"-tris (3-
methylphenylphenylamino)triphenylamine (generally called
MTDATA), which is a derivative of aromatic amine and

20   represented by the following structural formula (1):

[Structural formula (1)]
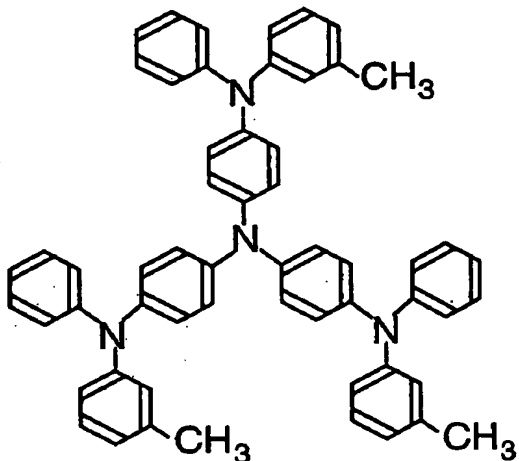
The MTDATA molecule is represented by a simplified chemical formula $C_{57}H_{48}N_4$ and its molar mass is 789.04 g/mol.

5   In the present example, the hole injecting and transporting layer 3 was formed to a thickness of 35 nm. Its thickness is generally within the range of 5 nm – 160 nm, preferably within the range of 25 nm – 70 nm.

In forming the hole injecting and transporting layer 3,

10   MTDATA was vapor deposited on a substrate at a rate of 0.10 $nm \cdot s^{-1}$. However, such a rate can be altered within the range from 0.0004 to 2.0 $nm \cdot s^{-1}$. A substrate temperature used to vapor deposit a constituent material of the hole injecting and transporting layer 3 can be altered within the range of

15   not exceeding 200 °C, but is preferably maintained not to exceed a glass transition temperature of the material used.

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In the case where such a material is MTDATA, it is
particularly preferred that a substrate temperature be
maintained within the range of not exceeding 100 ℃.

5   The luminescent layer 4 was formed from a mixture
containing, as a principal component (so-called "host"), N,
N'-diphenyl-N, N'-(3-methylphenyl)-1,1'-biphenyl-4, 4'-
diamine (generally called "TPD") which is a derivative of
aromatic amine and represented by the following structural
formula (2), and as a fluorescent dopant, 5, 6, 11, 12-

10   tetraphynylnaphthacene (generally called "rubrene") which is
an aromatic hydrocarbon compound represented by the
following structural formula (3):

[Structural formula (2)]

[structural formula (3)]

15
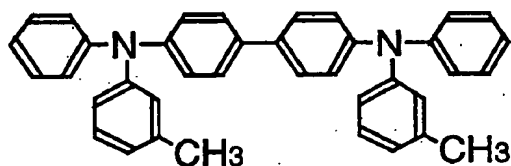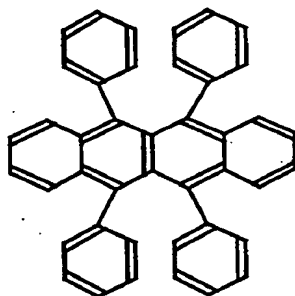
The dopant content was 5 % by mass. The dopant content
is generally in the range of 0.01 - 35 % by mass, preferably
in the range of 1.0 - 12 % by mass, more preferably in the
range of 2.5 - 7.5 % by mass. The luminescent layer 4 was

5   formed to a thickness of 16 nm. It is generally in the
range of 5 - 120 nm, preferably in the range of 11 - 55 nm.

The principal component of the luminescent layer 4,
i.e., the TPD molecule is represented by a simplified
chemical formula $C_{38}H_{32}N_2$ and its molar mass is 516.685 g/mol.

10   The fluorescent dopant present in the luminescent layer 4,
i.e., the rubrene molecule is represented by a simplified
chemical formula $C_{42}H_{28}$ and its molar mass is 532.68 g/mol.
In the present Example, a ratio in molar mass of the dopant
to host in the luminescent layer 4, i.e., rubrene to TPD

15   (dopant/host), was accordingly determined to be 1.0310. A
difference in molar mass between the dopant and host was
only about 3.1 %.

Each molecule to be deposited by a vacuum vapor
deposition technique can travel a distance according to its

20   mean free path determined on the basis of a physical
principle from a temperature of its evaporation source and
its molar mass. It is accordingly understood that the
behavior of each molecule in a vacuum, i.e., in a vapor
phase, is substantially governed by its molar mass. In this

25   Example, the dopant and host molecules are about equal in

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molar mass, and accordingly behave similarly in a vapor

phase, reach a substrate while forming a nearly perfectly

mixed molecular beam in the vapor phase, and change to a

solid phase. This enables formation of the luminescent

5   layer 4 in which the dopant and host molecules are mixed in

an ideal fashion.

On the other hand, if there exists a large difference

in molar mass between dopant and host molecules, the one

molecule having a lower molar mass, either dopant or host,

10   travels at a relatively higher linear speed, compared to the

other molecule. It is microscopically viewed that these two

types of molecules form molecular beams distinct from each

other and, after being changed into solids on the substrate,

tend to result in independently localized concentrations.

15   It is therefore understood that the dopant and host, if

their molar masses differ greatly from each other, will fail

to produce the luminescent layer 4 in which they are mixed

in an ideal manner.

In the formation of the luminescent layer 4 on the

20   substrate, an overall deposition rate of TPD and rubrene was

set at 0.10 $nm \cdot s^{-1}$. This rate can be altered within the

range of 0.0004 - 2.0 $nm \cdot s^{-1}$. While possible to be altered

within the range of not exceeding 200 ℃, a substrate

temperature is preferably controlled not to exceed any of

25   the glass transition temperatures of materials used to form

-32-

the hole injecting and transporting layer 3 or the luminescent layer 4. In the case where TPD is used, it is particularly preferred that a substrate temperature be controlled within the range of not exceeding 80 °C.

5   The electron injecting and transporting layer 5 was formed from bis(10-hyroxybenzo[h]quinolinate)beryllium (generally called "Bebq") as represented by the following structural formula (4):

[Structural formula (4)]
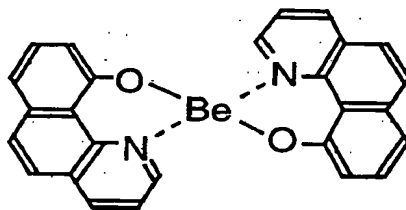
10   The electron injecting and transporting layer 5 was formed to a thickness of 38 nm. It is generally in the range of 5 nm - 160 nm, preferably in the range of 25 nm - 70 nm. The Bebq molecule is also represented by a simplified chemical formula $C_{26}H_{16}N_2O_2Be$ and its molar mass is

15   397.44 g/mol.

In the formation of the electron injecting and transporting layer 5 on the substrate, a deposition rate of Bebq was set at 0.10 $nm \cdot s^{-1}$. This rate can be altered within the range of 0.0004 - 2.0 $nm \cdot s^{-1}$. While possible to be

20   altered within the range of not exceeding 200 °C, a

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substrate temperature is preferably controlled not to exceed

any of the glass transition temperatures of materials used

to form the hole injecting and transporting layer 3, the

luminescent layer 4 or the electron injecting and

5   transporting layer 5. Where TPD is used, it is particularly

preferred that a substrate temperature be maintained within

the range of not exceeding 80 °C.

Formation of a negative electrode

After the organic EL layer 8 consisting of the hole

10   injecting and transporting layer 3, luminescent layer 4 and

electron injecting and transporting layer 5 has been formed

on the substrate, a negative electrode 6 is formed. The

negative electrode 6 is formed to such a predetermined

pattern as to intersect the patterned transparent positive

15   electrode by vapor depositing constituent materials under

vacuum with the aid of a shadow mask made of stainless

steel.

In the formation of the negative electrode 6, such

constituent materials are vapor deposited at a surrounding

20   pressure reduced to about 0.1 mPa at a substrate temperature

of 25 °C. The negative electrode 6 was formed to a

thickness of 300 nm. A thickness of the negative electrode

6 is generally in the range of 50 nm - 500 nm.

Ce, as the "f" element having an electronegativity value

25   higher than that of calcium, and, equal to or lower than

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that of vanadium, Al, as the "p" element having an

electronegativity value equal to or higher than that of

aluminum, lower than that of carbon, and lower than that of

iodine, and Ni, as the "f" element having an

5   electronegativity value equal to or higher than any of those

of iron, cobalt and nickel, and, equal to or lower than that

of gold, were vapor codeposited, while controlling a rate of

evaporation of each element from its evaporation source by

using a quartz oscillator-type film thickness monitoring

10   equipment, to form an alloy-like compound or mixture which

contained, by mass, 1.0 % Ce, 95 % Al and 4.0 % Ni.   The

negative electrode was formed from this alloy-like compound

or mixture.   The unit "% by mass", as used herein, is a

percentage representing each element content calculated on

15   the basis of mass.

Ce, Al and Ni have the following electronegativity

values; Ce (1.1 - 1.2: the first decimal place value was

undecided because of its inclusion of errors in

measurement), Al (1.5) and Ni (1.8).

20   Each element has the following atomic weight; Ce

(140.115 g/mol), Al (26.981539 g/mol) and Ni (58.6934

g/mol).

Conversion of the aforementioned proportion in mass of

Ce, Ni and Al to the proportion in the number of atoms of

25   Ce, Ni and Al gives {1 mass %/(140.115 g/mol)}:{4 mass

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%/(58.6934 g/mol)}:{95 mass %/(26.981539 g/mol)}, i.e.,

(0.198 atomic %):(1.90 atomic %):(97.9 atomic %). The unit

"atomic %", as used herein, is a percentage representing each

element content calculated on the basis of the number of

5   atoms.

The calculation of a mean electronegativity value E_{ave}

from weighting an electronegativity value of each element by

the above-given proportion in number of its atoms present in

the aforementioned negative electrode 6 resulted in

10   obtaining E_{ave} = 1.50, assuming that an electronegativity

value of Ce is 1.15.

The "f" element content, i.e., the Ce content by mass

can be altered within the range of 0.001 % - 35 %,

preferably within the range of 0.1 % - 10 %, more preferably

15   within the range of 0.3 % - 3 %. The "d" element content,

i.e., the Ni content by mass can be altered within the range

of 0 % - 99.9 %, preferably within the range of 0.1 % - 50

%, more preferably within the range of 1 % - 15 %. It is

preferred that a ratio (d/f) by mass of the element "d" to

20   the element "f" contained in the mixture is not below 2.

In the formation of the negative electrode 6 on the

substrate, deposition of each element was set at the

following rate; Ce (3.0 ng·cm^{-2}·s^{-1}), Al (285 ng·cm^{-2}·s^{-1}) and

Ni (12.0 ng·cm^{-2}·s^{-1}). For the evaporation sources of Al and

25   Ni, their respective simple substances, i.e., pure metals

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were used. On the other hand, an Al alloy containing 5 % by mass of Ce was used as the evaporation source of Ce. The deposition rate of Al onto the substrate can be altered generally within the range of 1.0 - 5,100 $ng \cdot cm^{-2} \cdot s^{-1}$,

5   preferably within the range of 60 - 1,100 $ng \cdot cm^{-2} \cdot s^{-1}$. The deposition rates of the other elements can be determined based on their desired contents by mass in the resulting mixture.

A simple substance of each element has the following

10   density at room temperature; Ce (6.8 g/cm^3), Al (2.69 g/cm^3) and Ni (8.85 g/cm^3). Accordingly, the negative electrode 6 is assumed to have a density of about 2.8 g/cm^3.

In the present Example, the negative electrode 6 was formed using a vacuum vapor deposition technique. However,

15   other techniques, such as a sputtering technique, can also be employed. For example, the negative electrode may be sputter formed by using, as a target, a compound and/or mixture containing the "f" and "p" elements, or, a compound and/or mixture containing the "f", "p" and "d" elements.

20   Formation of a protective film

The protective film 7 was formed from silicon monoxide (SiO) to a thickness of 200 nm. Its thickness is generally not below 20 nm, preferably in the range of 80 nm - 500 nm, and can be altered depending upon the typ of material used.

25   The protective film 7 was applied by using a vacuum vapor

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deposition technique. A source material to form the

protective film 7 was vapor deposited on the substrate at a

rate of 0.5 nm·s^{-1}. This deposition rate can be altered

within the range of 0.002 - 10 nm·s^{-1}. The source material

5   is preferably electrically insulative. The provision of

this protective film 7 is purposed to suppress modification

of the negative electrode 6 or organic EL layer 8 as by

moisture or oxygen. It should be recognized, however, that

the protective film 7 is not necessarily incorporated in the

10   organic EL device of the present invention.

Evaluation of performance characteristics of the organic EL

device

        The organic EL device, as fabricated in the manner as

described above, was observed to emit yellow light when an

15   DC voltage of 5.0 V was applied thereto. Conceivably, this

yellow radiation was emitted when rubrene was relaxed from

its excited state. The emissive luminance L_{5V} achieved 500

cd/m^2, and the emission efficiencies were 10.9 cd/A and 6.9

ℓm/w.

20   Also, the emission efficiencies were 11.7 cd/A and 10.1

ℓm/w when the emissive luminance dropped to 100 cd/m^2.

        The device was placed in the dry air having a 20 % or

lower relative humidity and operated by an DC constant

current such that a current density was maintained constant

25   at 46 A/m^2. An initial luminance was 500 cd/m^2. After the

-38-

lapse of 100 hours, the luminance dropped to 400 cd/m^2. Accordingly, a luminance ratio R_{100h}, a ratio of the initial luminance to the luminance after the lapse of 100 hours, was stopped at 80 %.

After the lapse of 500 hours, the luminance dropped to 350 cd/m^2. Accordingly, a luminance ratio R_{500h}, a ratio of the initial luminance to the luminance after the lapse of 500 hours, was stopped at 70 %. No appreciable dark spot was observed.

Also, the device was left in the air having a relative humidity of 55 - 65 % and a temperature of 20 - 30 ℃ for 500 hours and then driven to emit light. No appreciable dark spot was observed. The device exhibited uniform light emission.

EXAMPLES 2 - 32

The procedure of Example 1 was followed, except that mixtures and/or compounds containing different types and amounts of "f", "p" and "d" elements as listed in Tables 1 through 5 were used for negative electrodes, to fabricate organic EL devices.

For each organic EL device, the emissive luminance L_{5v} was measured when the applied DC voltage was 5 V. Each device was also placed in the dry air having a 20 % or lower relative humidity and operated by an DC constant current such that a current density was kept constant. The initial

-39-

luminance was 500 cd/m^2. This DC constant current operation was continued and the emissive luminance L_{500h} after the lapse of 500 hours was measured. A luminance ratio R_{500h}, a ratio of the initial luminance to the luminance after the lapse of

5   500 hours, was calculated based on the measured L_{500h} value.

In Tables 1 through 5, the mean electronegativity value E_{ave}, emissive luminance L_{5v} and luminance ratio R_{500h}, as measured and calculated for each device, are given.

In Example 30, a mixture and/or compound excluding the

10   "d" element but containing 1.0 % by mass of Ce, as the "f" element, and 99.0 % by mass of Sb, as the "p" element, was used for a negative electrode. Likewise, Example 31 used a mixture and/or compound having a composition excluding the "d" element for a negative electrode.

15

Table 1

Example No.	COMPOSITION, CONTENT (MASS%) [ATOMIC%]			E_{ave}	L_{5V} (cd/m^2)	R_{500h} (%)
	f	p	d			
1	Ce 1.0% [0.20%]	Al 95.0% [97.9%]	Ni 4.0% [1.90%]	1.50	500	70
2	Ce 0.30% [0.06%]	Al 98.7% [99.5%]	Ni 1.0% [0.46%]	1.50	320	68
3	Ce 3.0% [0.62%]	Al 88.0% [94.9%]	Ni 9.0% [4.46%]	1.51	520	63
4	Ce 6.0% [1.32%]	Al 79.0% [90.8%]	Ni 15.0% [7.92%]	1.52	540	31
5	Ce 9.0% [2.09%]	Al 73.0% [87.9%]	Ni 18.0% [9.97%]	1.52	430	11
6	Ce 1.0% [0.19%]	Al 98.9% [99.8%]	Ni 0.10% [0.05%]	1.50	470	6
7	Ce 1.0% [0.27%]	Al 49.0% [67.9%]	Ni 50.0% [31.8%]	1.59	360	58

5

10

Table 2

Example No.	COMPOSITION, CONTENT (MASS%) [ATOMIC%]			E_{ave}	L_{5V} (cd/m^2)	R_{500h} (%)
	f	p	d			
8	Ce 1.0% [0.20%]	Al 95.0% [97.9%]	Co 4.0% [1.89%]	1.50	480	68
9	Ce 1.0% [0.20%]	Al 95.0% [98.0%]	Cu 4.0% [1.75%]	1.51	470	63
10	Ce 1.0% [0.20%]	Al 95.0% [98.8%]	Ag 4.0% [1.04%]	1.50	490	70
11	Ce 1.0% [0.83%]	Sb 94.0% [89.4%]	Co 5.0% [9.82%]	1.88	270	36
12	Ce 1.0% [0.46%]	Sb 1.0% [0.53%]	Cu 98.0% [99.0%]	1.90	250	38
13	Ce 1.0% [0.87%]	Sb 98.0% [98.5%]	Au 1.0% [0.62%]	1.90	280	22
14	Ce 1.0% [0.87%]	Sb 95.0% [94.6%]	Pd 4.0% [4.56%]	1.91	290	33

5

10

Table 3

Example No.	COMPOSITION, CONTENT(MASS%) [ATOMIC%]			E_{ave}	L_{5v} (cd/m^2)	R_{500h} (%)
	f	p	d			
15	Ce 0.50% [0.38%]	Si 0.40% [1.52%]	Ag 99.1% [98.1%]	1.90	280	41
16	Ce 0.50% [0.38%]	Ge 0.40% [0.59%]	Ag 99.1% [99.0%]	1.90	270	38
17	Ce 0.50% [0.21%]	C 0.10% [0.49%]	Co 99.4% [99.3%]	1.80	310	48
18	Ce 0.50% [0.21%]	N 0.10% [0.42%]	Ni 99.4% [99.4%]	1.80	290	43
19	Ce 1.50% [0.21%]	S 0.20% [0.37%]	Ni 99.3% [99.4%]	1.80	280	32
20	Ce 0.50% [0.21%]	O 0.20% [0.73%]	Ni 99.3% [99.1%]	1.81	260	26
21	Ce 0.50% [0.21%]	Se 0.20% [0.15%]	Ni 99.3% [99.6%]	1.80	270	29

5

10

Table 4

Example No.	COMPOSITION, CONTENT (MASS%) [ATOMIC%]			E_{ave}	L_{5V} (cd/m^2)	R_{500h} (%)
	f	p	d			
22	Ce 0.50% [0.21%]	Te 0.20% [0.09%]	Ni 99.3% [99.7%]	1.80	260	28
23	Be 1.0% [3.00%]	Al 95.0% [95.2%]	Ni 4.0% [1.84%]	1.51	380	62
24	Sc 1.0% [0.62%]	Al 95.0% [97.5%]	Ni 4.0% [1.89%]	1.50	390	65
25	Y 1.0% [0.31%]	Al 95.0% [97.8%]	Ni 4.0% [1.89%]	1.50	410	66
26	Sm 1.0% [0.18%]	Al 95.0% [97.9%]	Ni 4.0% [1.90%]	1.51	480	69
27	Eu 1.0% [0.18%]	Al 95.0% [97.9%]	Ni 4.0% [1.90%]	1.51	470	68

5

10

Table 5

Example No.	(mass%) [atomic%]			E_{ave}	L_{5V} (cd/m^2)	R_{500h} (%)
	f	p	d			
28	Er 0.30% [0.05%]	Al 98.7% [99.5%]	Ni 1.0% [0.46%]	1.50	310	61
29	Yb 0.30% [0.05%]	Al 98.7% [99.5%]	Ni 1.0% [0.46%]	1.50	290	58
30	Ce 1.00% [0.87%]	Sb 99.0% [99.1%]	None	1.89	210	20
31	Ce 3.00% [0.59%]	Al 97.0% [99.4%]	None	1.50	480	3
32	Ce 0.50% [0.21%]	B 0.10% [0.54%]	Co 99.4% [99.2%]	1.80	320	49

COMPARATIVE EXAMPLES 1 - 10

The procedure of Example 1 was followed, except that mixtures and/or compounds having different compositions (containing different combinations and amounts of the "a", "b" and "c" elements) as listed in Tables 6 and 7 were used as negative electrode materials, to fabricate comparative organic EL devices.

In the same manner as stated above, the comparative organic EL devices obtained were evaluated for performance characteristics. The results are given in the following Tables 6 and 7.

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Table 6

Comp. Example No.	COMPOSITION, CONTENT(MASS%) [ATOMIC%]			E_{ave}	L_{5V} (cd/m^2)	R_{500h} (%)
	a	b	c			
1	Ce 100.0% [100.0%]	None	None	1.15	0	0
2	Al 100.0% [100.0%]	None	None	1.50	0	0
3	Ni 100.0% [100.0%]	None	None	1.80	0	0
4	Ce 1.0% [0.42%]	Ni 99.0% [99.6%]	None	1.80	90	9
5	Mg 100.0% [100.0%]	None	None	1.20	0	0
6	Ag 100.0% [100.0%]	None	None	1.90	0	0
7	Mg 69.2% [90.9%]	Ag 30.8% [9.1%]	None	1.26	190	8

5

10

Table 7

Comp. Example No.	COMPOSITION, CONTENT(MASS%) [ATOMIC%]			E_{ave}	L_{5V} (cd/m^2)	R_{500h} (%)
	a	b	c			
8	Li 100.0% [100.0%]	None	None	1.00	0	0
9	Li 0.50% [1.9%]	Al 99.5% [98.1%]	None	1.49	240	0
10	Li 0.09% [0.4%]	Mg 72.5% [91.8%]	Ag 27.4% [7.8%]	1.25	210	9

As apparent from the comparison of the results of Examples shown in Tables 1 through 5 to the results of Comparative Examples shown in Tables 6 and 7, the organic EL devices, in accordance with the present invention, exhibit the increased levels of emissive luminance and the reduced levels of luminance drop after long-term operation.

EXAMPLE 33

The procedure of Example 1 was followed, except that the luminescent layer 4 contained 5.0 % by mass of naphthacene as a luminescent dopant, instead of rubrene, to fabricate an organic EL device. Like rubrene, naphthacene is an aromatic compound structurally represented as four benzene rings serially fused together. However, unlike rubrene, naphthacene contains no phenyl group. Naphthacene

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is represented by the following structural formula (5):

[Structural Formula (5)]
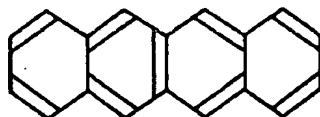
The above-fabricated organic EL device was observed to emit yellow light when an applied DC voltage was 5.0 V. Conceivably, this yellow radiation was emitted when naphthacene was relaxed from its excited state. The emissive luminance L_{5v} achieved 327 cd/m^2, and the emission efficiencies were 7.1 cd/A and 4.8 ℓm/w. Also, the emission efficiencies were 7.3 cd/A and 5.2 ℓm/w when the emissive luminance was dropped to 100 cd/m^2.

The device was placed in the dry air having a 20 % or lower relative humidity and operated by an DC constant current such that a current density was held constant. An initial luminance was 500 cd/m^2. After the lapse of 100 hours, the luminance dropped to 323 cd/m^2. Accordingly, a luminance ratio R_{100h}, a ratio of the initial luminance to the luminance after the lapse of 100 hours, was stopped at 64 %. After the lapse of 500 hours, the luminance dropped to 251 cd/m^2. Accordingly, a luminance ratio R_{500h}, a ratio of the initial luminance to the luminance after the lapse of 500 hours, was stopped at 50 %. No appreciable dark spot was

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observed.   Also, the device was left in the air having a

relative humidity of 55 - 65 % and a temperature of 20 - 30

°C for 500 hours and then driven to emit light.   No

appreciable dark spot was observed.   The device exhibited

5   uniform light emission.

The fluorescent dopant present in the luminescent layer

4, i.e., the naphthacene molecule is represented by a

simplified chemical formula $C_{18}H_{12}$ and its molar mass is

228.29 g/mol.   It can be pointed out that in the present

10   Example, a ratio in molar mass of the dopant to host in the

luminescent layer 4, i.e., naphthacene to TPD (molar mass =

516.685 g/mol) was 0.44184 and the molar mass of the host

molecule was about 2.263 times greater than that of the

dopant molecule.

15   **EXAMPLE 34**

The procedure of Example 1 was followed, except that

the luminescent layer 4 contained 5.0 % by mass of

anthracene as a luminescent dopant, instead of rubrene, to

fabricate an organic EL device.   Anthracene is an aromatic

20   compound structurally represented as three benzene rings

serially fused together.   However, anthracene contains no

phenyl group, unlike rubrene.   Anthracene is represented by

the following structural formula (6):

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[Structural Formula (6)]
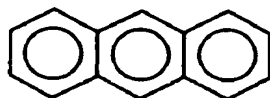
The above-fabricated organic EL device was observed to
emit blue light when an DC voltage of 5.0 V was applied
thereto. This blue radiation was conceivably emitted when

5   anthracene was relaxed from its excited state. The emissive
luminance L_{5V} achieved 317 cd/m^2, and the emission
efficiencies were 6.9 cd/A and 4.6 ℓm/w. Also, the emission
efficiencies were 7.0 cd/A and 4.7 ℓm/w when the emissive
luminance was dropped to 100 cd/m^2.

10   The device was placed in the dry air having a 20 % or
lower relative humidity and operated by an DC constant
current such that a current density was held constant. An
initial luminance was 500 cd/m^2. After the lapse of 100
hours, the luminance dropped to 192 cd/m^2. Accordingly, a

15   luminance ratio R_{100h}, a ratio of the initial luminance to the
luminance after the lapse of 100 hours, was stopped at 38 %.
After the lapse of 500 hours, the luminance dropped to 45
cd/m^2. Accordingly, a luminance ratio R_{500h}, a ratio of the
initial luminance to the luminance after the lapse of 500

20   hours, was stopped at 9 %. A number of appreciable dark
spots were observed. Also, the device was left in the air

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having a relative humidity of 55 - 65 % and a temperature of 20 - 30 °C for 500 hours and then driven to emit light. No appreciable dark spot was observed. The device exhibited uniform light emission.

5   The fluorescent dopant present in the luminescent layer 4, i.e., the anthracene molecule is represented by a simplified chemical formula $C_{14}H_{10}$ and its molar mass is 178.23 g/mol. It can be pointed out, accordingly, that in the present Example, a ratio in molar mass of the dopant to

10   host in the luminescent layer 4, i.e., anthracene to TPD (molar mass = 516.685 g/mol) was 0.34495, and the molar mass of the host molecule was about 2.899 times greater than that of the dopant molecule.

       As apparent from the results obtained in Examples 33

15   and 34, the organic EL device according to the present invention, even if the type of the fluorescent dopant in its luminescent layer is changed, exhibits the increased level of emissive luminance and the reduced level of luminance drop after long-term operation.

20   The organic EL layer was illustrated in the above Examples as having a structure consisting of the hole injecting and transporting layer, luminescent layer and electron injecting and transporting layer. However, the present invention is not limited to such a multilayer

25   structure, and can be applied to the other types of

multilayer structures. Also, the materials used in the above Examples, such as luminescent materials, dopant materials, hole transporting materials, electron transporting materials, positive electrode materials and

5   other materials, are not intended to limit the present invention. Furthermore, other manufacturing processes can be used if applicable to the present invention.

EXAMPLE 35

Figure 2 is a sectional view, showing a construction of

10   an organic EL device of Example 35. Referring to Figure 2, a glass substrate 11 is shown to carry a transparent positive electrode 12 thereon. In the fabrication of a display with light emitting elements arranged in a matrix pattern, a parallel set of strip-form transparent positive

15   electrodes 12 may be pattern formed on the glass substrate 11. A sequence of a hole injecting layer 13a, a hole transporting layer 13b, a luminescent layer 14, each formed of organic material, overlies the transparent positive electrode 2. The hole injecting layer 13a, hole

20   transporting layer 13b and luminescent layer 4 constitute an organic EL layer 18. Overlying the luminescent layer 14 is a negative electrode 16 which consists of a first layer 16a positioned on the luminescent layer 14, a second layer 16b on the first layer 16a and a third layer 16c on the second layer 16b.

25   layer 16b. The negative electrode 16 is covered with a

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protective layer 17.

A manufacturing process of the organic EL device of the present embodiment will be now explained.

Fabrication of a transparent positive electrode

5   In the similar manner as in Example 1, a parallel set of stip-form transparent electrodes 12 was pattern formed on the glass substrate 1. In this Example, the patterned transparent positive electrode 2 was formed from indium tin oxide (ITO) to an average thickness of 200 nm.

10   Formation of an organic EL layer

The hole injecting layer 13a, hole transporting layer 13b and luminescent layer 14 were sequentially stacked on the glass substrate 11 carrying the patterned transparent positive electrode 12 by a vacuum vapor deposition

15   technique. The hole injecting layer 13a, hole transporting layer 13b and luminescent layer 14 were vapor deposited at a surrounding pressure reduced to about 0.1 mPa at a substrate temperature of 25 °C.

The hole injecting layer 13a was formed from copper

20   (II) phthalocyanine (generally called CuPc), as represented by the following structural formula (7):
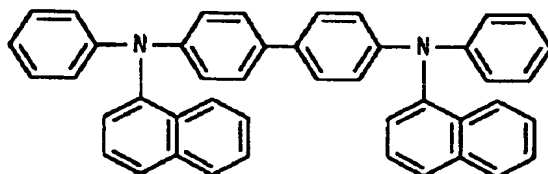
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[Structural formula (7)]
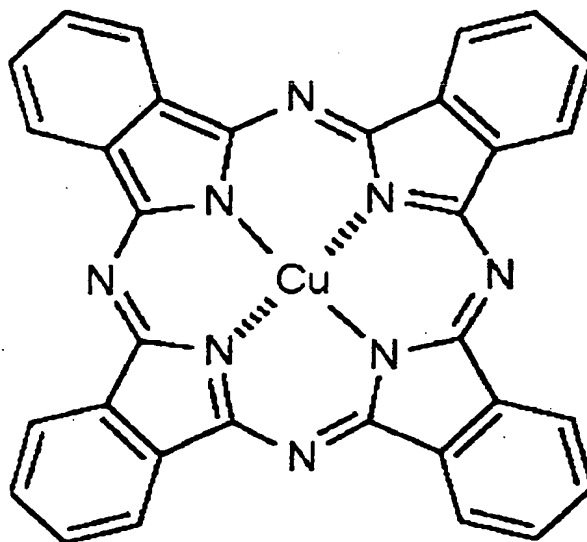
In the present Example, the hole injecting layer 13a was formed to a thickness of 10 nm. The CuPc molecule is

5   represented by a simplified chemical formula $C_{32}H_{16}N_8Cu$ and its molar mass is 576.08 g/mol.

The hole transporting layer 13b was formed from N, N'-di-1-naphthalenyl-N, N'-diphenyl-(1, 1'-biphenyl)-4, 4-diamine (generally called "NPB"), as represented by the

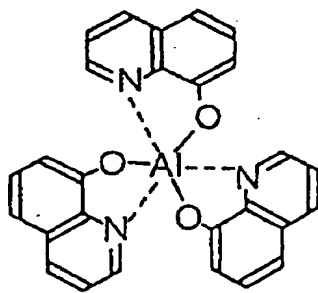10   following structural formula (8):

[Structural Formula (8)]

In the present Example, the hole transporting layer 13b was formed to a thickness of 80 nm. The NPB molecule is represented by a simplified chemical formula $C_{44}H_{32}N_2$ and its molar mass is 588.0 g/mol.

The luminescent layer 14 was formed from aluminum tris(quinoline-8-olate) (generally called "Alq$_3$") as represented by the following structural formula (9):

[Structural Formula (9)]

In the present Example, the luminescent layer 14 was formed to a thickness of 40 nm. The Alq$_3$ molecule is represented by a simplified chemical formula $C_{27}H_{18}N_3O_3Al$ and its molar mass is 459.44 g/mol.

Formation of a negative electrode

After formation on the glass substrate 11 of the
organic EL layer 18 consisting of the hole injecting layer
13a, hole transporting layer 13b and luminescent layer 14, a
negative electrode 16 are formed. The negative electrode 16

5   is formed in such a predetermined pattern as to intersect
the patterned transparent positive electrode 12 by vapor
depositing constituent materials under vacuum with the aid
of a shadow mask made of stainless steel. The negative
electrode 16 is formed by stacking on the luminescent layer

10   14, in sequence, the first negative electrode layer 16a,
second negative electrode layer 16b and third negative
electrode layer 16c.

The first negative electrode layer 16a was
substantially formed from Ce as the "f" element. The first

15   negative electrode layer 16a was vapor deposited at a
surrounding pressure reduced to about 0.1 mPa at a substrate
temperature of 25 °C. In this Example, the first negative
electrode layer 16a was formed to a thickness of 1 nm. A
thickness of the first negative electrode layer 16a is

20   preferably up to 5 nm, more preferably in the range of 0.1 -
5 nm. Ce is the most abundant element, among rare-earth
elements, and is present in the concentration of 46 ppm in
the earth crust. Ce is thus considered to have the least
potential of depletion among the rare-earth elements. Ce

25   has an atomic weight of 140.12 g/mol which is not too high

but is close in level to Ba (atomic weight = 137.323 g/mol),
one of alkaline earth metals. This preferred atomic weight
level makes Ce suitable for use in the formation of high-
quality thin-film negative electrodes by a sputtering or

5   vacuum vapor deposition technique. According to a
literature, a vapor pressure of Ce is 0.1333 Pa at 1,572 °C,
1.333 Pa at 1,737 °C and 13.33 Pa at 1,947 °C. In the
formation of negative electrodes by a vacuum vapor
deposition technique, this relatively high level in vapor

10 pressure of Ce permits deposition at temperatures of not
exceeding 2,000 °C. Also, because of its low
electronegativity value, the inclusion of Ce in the negative
electrode facilitates electron injection into the organic EL
layer 18. For the reasons as stated above, the present

15 Example used Ce for the first negative electrode layer 16a.

       The second negative electrode layer 16b has such a
composition gradient in its thickness direction that toward
its interface with the third negative electrode layer 16c
from its interface with the first negative electrode layer

20 16a, its "f" element content, i.e., Ce content decreases
while its "p" element content, i.e., Al content increases.
The second negative electrode layer 16b contained 100 % by
mass of Ce at its interface with the first negative
electrode layer 16a, and 7.5 % by mass of Ce and 92.5 % by

25 mass of Al in the vicinity of its interface with the third

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negative electrode layer 16c. Specifically, Ce and Al were vapor codeposited at a surrounding pressure reduced to about 0.1 mPa at a substrate temperature of 25 °C, while controlling a rate of evaporation of each element from its

5   evaporation source by using a quartz oscillator-type film thickness monitoring equipment, to form the second negative electrode layer 13b having such a predetermined composition gradient in its thickness direction. In the present Example, the second negative electrode layer 16b was formed

10   to a thickness of 20 nm. A thickness of the second negative electrode layer 16b is generally in the range of 1 - 40 nm.

The third negative electrode layer 16c is substantially formed from Al as the "p" element. The third negative electrode layer 16c is vapor deposited at a surrounding

15   pressure reduced to about 0.1 mPa at a substrate temperature of 25 °C. In this Example, the third negative electrode layer 16c was formed to a thickness of 300 nm. A thickness of the third negative electrode layer 16c is generally in the range of 50 - 400 nm. Al, constituting the third

20   negative electrode layer 16c, has an electrical resistivity of 2.655 $\mu \Omega$ cm, and is more electrically conductive compared to Ce (electrical resistivity = 75.0 $\mu \Omega$ cm). The increased thickness of the third negative electrode layer 16c thus serves to reduce the overall electrical resistance of the

25   negative electrode 16.

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In this Example, the second negative electrode layer
16b having the aforementioned graded composition is
interposed between the first negative electrode layer 16a
substantially formed of Ce and the third negative electrode

5   layer 16c substantially formed of Al. This construction
assures good adhesion between the first and second negative
electrode layers 16a and 16b and also between the second and
third negative electrode layers 16b and 16c, leading to the
reduced occurrence of delamination and to the relaxation of

10   heat shock due to the difference in thermal expansibility
between Ce and Al.

In this Example, the first negative electrode layer 16a
is substantially formed from Ce, as the "f" element, the
third negative electrode layer 16c from Al, as the "p"

15   element, and the second negative electrode layer 16b from
the aforementioned "f" and "p" elements, i.e., Ce and Al, such
that it has a composition gradient in its thickness
direction. However, the present invention is not limited to
such a construction. An additional element may further be

20   included in at least one of the first, second and third
negative electrode layers 16a, 16b and 16c.

The additional element may preferably be at least one
element, "d", selected from those having electronegativity
values equal to or higher than any of those of iron, cobalt

25   and nickel, and, equal to or lower than that of gold.

However, the selection in type of such an additional element may be suitably made depending upon the particular purpose contemplated.

The following illustrates a possible negative electrode construction incorporating such an additional element.

The first negative electrode layer 16a is formed substantially from Yb, as the "f" element, and Zn, as the second "p" element, such that it contains, on average, 50 % by mass of Yb and 50 % by mass of Zn. The second negative electrode layer 16b is formed substantially from Yb, as the "f" element, Zn, as the second "p" element, and Al, as the first "p" element, such that the second negative electrode layer 16b defines a composition gradient in its thickness direction, specifically, contains, on average, 50 % by mass of Yb, 50 % by mass of Zn and 0 % by mass of Al at its interface with the first negative electrode layer 12a, and 0 % by mass of Yb, 0 % by mass of Zn and 100 % by mass of Al in the vicinity of its interface with the third negative electrode layer 16c. The third negative electrode layer 16c is formed substantially solely from Al, as the first "p" element.

Formation of a protective film

Analogous to Example 1, a protective film 17 was formed from silicon monoxide (SiO) to a thickness of 300 nm.

COMPARATIVE EXAMPLE 11

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The procedure of Example 35 was followed, except that the negative electrode 16 was constructed in a single layer (300 nm thick) of an Mg-In alloy (containing 90 % by mass of Mg and 10 % by mass of In), to form a comparative organic EL device.

Evaluation of performance characteristics of the organic EL devices

The organic EL devices of Example 35 and Comparative Example 11, as respectively fabricated in the manners as stated above, were measured for initial luminance and initial emission efficiency when an applied DC voltage was 14 V. The measurement results are given in the following Table 8.

Table 8

	INITIAL LUMINANCE at 14V (cd/m^2)	INITIAL EMISSION EFFICIENCY at 14V	
		(cd/A)	(ℓm/w)
Example 35	7.0×10^3	2.50	0.56
Comp. Example 11	1.4×10^4	0.91	0.20

As can be seen from Table 8, the organic EL device of Example 35 according to the present invention exhibited the increased initial efficiency of light emission, compared to the organic EL device of Comparative Example 11.

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Also, each device was placed in the dry air having a 20
% or lower relative humidity and operated by an DC constant
current such that an operating current density was held
constant at 100 A/m^2, and measured for luminance, emission
efficiency and chromaticity, both initially and after the
lapse of 500 hours. The measurement results are given in
the following Table 9.

Table 9

	LAPSE OF TIME (h)	VOLTAGE (V)	LUMINANCE (cd/m^2)	EMISSION EFFICIENCY		CHROMATICITY	
				(cd/A)	(ℓm/w)	CIE-x	CIE-y
Example 35	0	9.3	120	1.20	0.41	0.29	0.59
	500	12.4	78	0.78	0.20	0.29	0.59
Comp. Example 11	0	9.5	107	1.07	0.35	0.31	0.58
	500	13.9	51	0.51	0.12	0.32	0.59

As can be appreciated from Table 9, the organic EL
device of Example 35 according to the present invention
exhibited higher levels of luminance and emission
efficiency, both initially and after 500 hours, compared to
the organic EL device of Comparative Example 11, and showed
little change in chromaticity.

The organic EL layer of Example 35 was illustrated as
having a structure consisting of the hole injecting layer,

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hole transporting layer and luminescent layer. However, the present invention is not limited to such a multilayer structure, and can be applied to the other configurations of multilayer structures. Also, the materials used in Example

5   35, such as luminescent materials, hole injecting materials, hole transporting materials, electrode materials and other materials, are not intended to limit the present invention. Also, other manufacturing processes can alternatively be employed if applicable to the present invention.

10   In accordance with the organic EL device of the present invention, an improvement in emission efficiency can be achieved. Also, a voltage level required to obtain a desired emissive luminance can be lowered. This leads to the reduction in level of an operating voltage. Also, the

15   increased emissive luminance can be obtained when a given voltage is applied.

       Furthermore, a phenomena observed when light emission is continued at a given current density, i.e., the reduction of emissive luminance with the lapse of time, can be

20   suppressed to occur for at least a certain period of time. The emissive luminance that is obtained under the operation at a given current density and/or at a given voltage applied can thus be maintained at a level of not below a certain value over a long period of time. Therefore, a service life

25   of the device can be extended.